

# Analysis of Radium-226 in High Salinity Wastewater from Unconventional Gas Extraction by Inductively Coupled Plasma-Mass Spectrometry

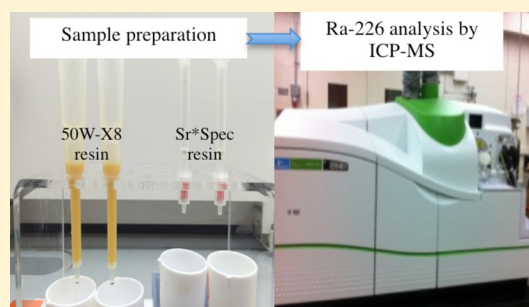
Tieyuan Zhang,<sup>†,§</sup> Daniel Bain,<sup>‡,§</sup> Richard Hammack,<sup>§</sup> and Radisav D. Vidic<sup>\*,†,§</sup>

<sup>†</sup>Department of Civil & Environmental Engineering and <sup>‡</sup>Department of Geology & Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States

<sup>§</sup>National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15236, United States

**S** Supporting Information

**ABSTRACT:** Elevated concentration of naturally occurring radioactive material (NORM) in wastewater generated from Marcellus Shale gas extraction is of great concern due to potential environmental and public health impacts. Development of a rapid and robust method for analysis of Ra-226, which is the major NORM component in this water, is critical for the selection of appropriate management approaches to properly address regulatory and public concerns. Traditional methods for Ra-226 determination require long sample holding time or long detection time. A novel method combining Inductively Coupled Mass Spectrometry (ICP-MS) with solid-phase extraction (SPE) to separate and purify radium isotopes from the matrix elements in high salinity solutions is developed in this study. This method reduces analysis time while maintaining requisite precision and detection limit. Radium separation is accomplished using a combination of a strong-acid cation exchange resin to separate barium and radium from other ions in the solution and a strontium-specific resin to isolate radium from barium and obtain a sample suitable for analysis by ICP-MS. Method optimization achieved high radium recovery ( $101 \pm 6\%$  for standard mode and  $97 \pm 7\%$  for collision mode) for synthetic Marcellus Shale wastewater (MSW) samples with total dissolved solids as high as 171,000 mg/L. Ra-226 concentration in actual MSW samples with TDS as high as 415,000 mg/L measured using ICP-MS matched very well with the results from gamma spectrometry. The Ra-226 analysis method developed in this study requires several hours for sample preparation and several minutes for analysis with the detection limit of 100 pCi/L with RSD of 45% (standard mode) and 67% (collision mode). The RSD decreased to below 15% when Ra-226 concentration increased over 500 pCi/L.



## 1. INTRODUCTION

Recent developments in horizontal drilling and hydraulic fracturing enabled efficient and economical extraction of natural gas from unconventional resources and has led to rapid expansion of gas extraction to meet global energy needs.<sup>1</sup> However, hydraulic fracturing generates a large volume of wastewater containing high concentrations of total dissolved solids (TDS), heavy metals, and naturally occurring radioactive material (NORM).<sup>1–5</sup> The wastewater generated during the initial period after the well completion (i.e., the first 2 weeks) is typically referred to as “flowback water”, and wastewater generated during the well production stage is termed “produced water”. This study refers to both as Marcellus Shale wastewater (MSW).

Radium-226 (i.e., Ra-226) is one of the major components of NORM in Marcellus Shale wastewater and is an important proxy for the radioactivity of waste streams generated during unconventional gas production.<sup>5</sup> Ra-226 has a very long half-life (1,620 years), resulting in an extended period of activity when brought to the surface. Ra-226 activity in wastewater from Marcellus Shale ranges from hundreds to tens of thousands

pCi/L and is often strongly correlated with total dissolved solids (TDS) in MSW that can be as high as 350,000 mg/L.<sup>2,4</sup> Several studies investigated the impact of shale gas development on surface water quality in Pennsylvania<sup>1,2,6</sup> and potential treatment options<sup>4,5</sup> for the highly contaminated wastewater generated by this industry. However, the challenging nature of NORM measurement limits our ability to design MSW management strategies to adequately resolve regulatory and public concerns stemming from high NORM content. Hence, the development of a rapid and robust method for NORM analysis in MSW, especially for Ra-226, is critical to advance our understanding of the fate of NORM and to develop the best NORM management practice for the unconventional gas industry.

The two approaches that are generally utilized to detect Ra-226 include 1) alpha spectrometry or liquid scintillation

**Received:** September 22, 2014

**Revised:** February 1, 2015

**Accepted:** February 2, 2015

**Published:** February 2, 2015

counting (LSC) to quantify the emission rates of alpha/beta particles, such as EPA Method 903.0 and 903.1 and 2) gamma spectrometry to quantify the emission rates of  $\gamma$  rays, such as EPA Method 901.1.<sup>6–14</sup> Alpha spectrometry often relies on Radon-222 (i.e., Rn-222) emanation and requires at least 3 weeks for the progeny to reach secular equilibrium (ingrowth period) with Ra-226 before sample analysis. Ra-226 can be directly quantified by alpha spectrometry at 4.8 MeV. However, due to the low penetrability of alpha particles, extensive sample preparation is needed to minimize sample thickness.<sup>15,16</sup> Gamma spectrometry utilizes sodium iodide (NaI) scintillation counter or high purity germanium (HPGe) detectors to quantify Ra-226 by analyzing its equilibrium progenies, such as Pb-214 and Bi-214. Indirect measurement of Ra-226 is often necessary in gamma spectrometry due to strong interference from U-235 near the 186 keV emission of Ra-226. It is possible to measure Ra-226 in wastewater from shale gas extraction without an ingrowth period because the interfering isotopes (i.e., U-235) are usually present at low concentrations. However, long counting times (24–48 h) for each sample are required for both alpha and gamma spectrometry to obtain accurate results, thereby limiting the sample throughput.<sup>5,14</sup>

Techniques using either thermal ionization mass spectrometry (TIMS) or inductively coupled plasma mass spectrometry (ICP-MS) to determine Ra-226 concentration have emerged in recent years.<sup>17–26</sup> These techniques utilize the increasing sensitivity of mass spectrometry. Modern spectrometry has detection limits as low as 0.1 ng/L (part per trillion), corresponding to Ra-226 concentration of 100 pCi/L or Ra-228 concentration of 23,000 pCi/L. In addition, highly efficient sample introduction systems can increase sensitivity up to ten times.<sup>22</sup>

Previous studies evaluated wet chemical purification procedures for radium extraction from low salinity solutions with reasonable radium recovery (>80%).<sup>17–24</sup> Those techniques include solid-phase extraction using cation exchange resins, coprecipitation with sulfates, manganese dioxide (MnO<sub>2</sub>) pre-concentration, and 3M Empore RAD disks. However, radium recovery efficiencies of these procedures are greatly diminished in high salinity solutions due to high concentrations of competing ions.<sup>24</sup> Several studies successfully separated radium from seawater prior to ICP-MS or TIMS measurement.<sup>25,26</sup> For example, Hsieh et al. used the MnO<sub>2</sub> for radium adsorption prior to extraction by Sr–Ra–SO<sub>4</sub> coprecipitation, conversion to Sr–Ra–CO<sub>3</sub>, and followed by purification with 50W-X8 resin and Sr\*spec resin.<sup>25</sup> However, these procedures are not suitable for the MSW, which contains significantly higher concentrations of barium and other matrix components (e.g., calcium, strontium). A recent study evaluated the impact of matrix compounds in MSW on Ra-226 recovery by several wet chemical techniques (e.g., MnO<sub>2</sub> adsorption, Rad Disk) and concluded that the recovery may be as low as 1% due to very high ionic strength and barium concentration in MSW samples.<sup>9</sup> This study was designed to evaluate an alternative radium extraction/purification procedure for high salinity wastewater from Marcellus Shale in Pennsylvania to enable Ra-226 analysis by ICP-MS. The main focus of this study was to ensure high recovery and accurate detection of Ra-226 while minimizing the analysis time.

## 2. MATERIALS AND METHODS

**2.1. Reagents and Materials.** Bio-Rad 50W-X8 (100–230 mesh) cation exchange resin (Bio-Rad Laboratories) was

loaded into a 0.8 cm diameter polypropylene column with a 25 mL extension funnel (Eichrom Technologies, Lisle, IL). Sr\*Spec (100–150  $\mu$ m) resin (Eichrom Technologies) was purchased in prepackaged 1 mL cartridges. Radium-226 was obtained from the Pennsylvania State University in a Ra-226 stock solution and calibrated using a Canberra gamma spectrometry with broad energy germanium (BeGe) detector (BE2020). Other ACS-grade reagents included barium chloride dihydrate (99.0% min, Mallinckrodt Chemicals), strontium chloride hexahydrate (99.0%, Acros Organics), calcium chloride dihydrate (99.4%, Fisher Scientific), sodium chloride (99.8%, Fisher Scientific), trace metal grade nitric acid, (65–70%, Fisher Scientific), and trace metal grade hydrochloric acid (37.3%, Fisher Scientific). Deionized (DI) water was produced by a laboratory water purification system (Millipore, Billerica, MA, USA). All reagents were found to be free of Ra-226.

**2.2. Resin Preparation.** The polypropylene columns were cleaned by soaking in 3 M HNO<sub>3</sub> for 20 min prior to loading with 4 mL of 50W-X8 exchange resin. The resin was then conditioned with three bed volumes (12 mL) of 6 M HNO<sub>3</sub> to ensure that it is in the protonated form, washed with 5 bed volumes of DI water and 5 bed volumes of 2% HNO<sub>3</sub>, and stored in 2% HNO<sub>3</sub> before use. Spent 50W-X8 resin was also regenerated using this procedure.

The Sr\*Spec resin in prepackaged 1 mL cartridges can be regenerated at least once by washing with 10 mL of 6 M heated HCl followed by a rinse with 10 mL of DI water.<sup>26,27</sup>

**2.3. Marcellus Shale Wastewater Samples.** A synthetic Marcellus Shale wastewater sample containing 5 mM of BaCl<sub>2</sub> and SrCl<sub>2</sub>, 50 mM of CaCl<sub>2</sub>, 1 M of NaCl, and 50,000 pCi/L of Ra-226 was prepared to optimize the radium separation/purification procedure. Seven synthetic samples (S1–S7) that are representative of MSW containing 5,000 pCi/L of Ra-226 and varying levels of TDS were prepared to test radium recovery with both new and regenerated Sr\*Spec resin. Nine MSW field samples (1–9) containing varying levels of TDS and Ra-226 collected from unconventional gas wells and storage impoundments in southwest and northeast Pennsylvania were analyzed by the ICP-MS method and compared with the reference measurements by gamma spectrometry.

**2.4. Analytical Instruments.** The NexION 300x Inductively Coupled Plasma-Mass Spectrometry (PerkinElmer, Waltham, MA) was used to measure Ra-226 concentration both in standard mode and collision mode using a nonreactive helium gas and Kinetic Energy Discrimination (KED) process. Detection limit was determined to be 0.1 ng/L, which is equal to 100 pCi/L of Ra-226. Details of the instrument components, operating conditions, and data acquisition parameters are summarized in the Supporting Information (Table SI-1).

Concentrations of major cations (i.e., Na, Ca, Sr and Ba) in real MSW and their elution profiles were measured by atomic absorption spectrometry (PerkinElmer, Model 1000 AAS) with a nitrous oxide-acetylene flame. The eluent samples were diluted with 2% nitric acid and 0.15% KCl solution prior to analysis to limit interferences during metal analysis,<sup>2</sup> and the dilution ratios were chosen based on the linear range of the AAS. The reproducibility of this analytical procedure is within 5%.

The elution profile of Ra-226 for synthetic flowback water samples was also analyzed using Packard 2100 Liquid Scintillation Counter (LSC). The eluents from 50W-X8 and Sr\*Spec resin were collected in 5 or 0.5 mL volumes, respectively. These samples were evaporated to dryness,

Table 1. Impact of Matrix Elements on Apparent Ra-226 Recovery Measured by NexION 300 ICP-MS

interfering elements				ICP-MS results			
				standard mode		collision mode	
Na (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	apparent Ra-226 recovery (%)	RSD (%)	apparent Ra-226 recovery (%)	RSD (%)
1				98	2	96	13
5				101	3	98	15
10				99	6	96	0
	1			99	8	98	6
	10			93	4	91	4
	20			96	7	91	5
		1		100	5	92	12
		5		101	6	95	2
			1	100	8	97	6
			5	101	6	94	9
			10	105	7	94	8
			20	81	9		
			40	62	17		
1	1	1	1	104	3	91	9
1	5	0.1	2.5	109	8	107	14
5	10	0.1	5	101	4	94	9
5	10	0.1	10	106	4	108	5
5	15	0.1	10	104	9	103	4
10	30	0.1	10	106	6	95	8

redissolved in 5 mL of DI water and 5 mg of Ba<sup>2+</sup> carrier (i.e., 1.82 mL of 20 mmol BaCl<sub>2</sub> solution), and 20 mL of 1 M H<sub>2</sub>SO<sub>4</sub> was added to ensure complete barium removal by precipitation as barium sulfate (Barite). If there was already a significant concentration of barium in the sample, the addition of BaCl<sub>2</sub> was adjusted so that the total mass of barium in the sample did not exceed 5 mg to ensure complete dissolution of precipitated Barite in EDTA solution as discussed below. The sample was maintained at 80 °C for 1 h to ensure that all Ra-226 in solution is completely coprecipitated with BaSO<sub>4</sub>.<sup>31</sup> The precipitate was then collected on a 0.45 μm cellulose ester membrane (Millipore, Billerica, MA, USA) and transferred into a scintillation vial by washing with 2 mL of 0.25 M EDTA solution at pH 8–9. The sample was heated at 60 °C until the solution became transparent to ensure complete dissolution of Ra-BaSO<sub>4</sub> in EDTA solution. After the vial is cooled to room temperature, 14 mL of Ultima Gold universal LSC-cocktail was added and vigorously mixed with the sample.<sup>7</sup> The sample was then counted on LSC for 60 min in 170–230 keV energy range that is specific to Ra-226.<sup>28,29</sup>

A Canberra gamma spectrometry system with a broad energy Germanium (BeGe) detector (Be 2020) was used to quantify Ra-226 activity.<sup>4,8,14</sup> Ra-226 activity in real Marcellus Shale wastewater samples was quantified by measuring gamma ray emission from the progenies of Ra-226 (Bi-214 and Pb-214) after waiting for at least 21 days to achieve secular equilibrium.

### 3. RESULTS AND DISCUSSION

**3.1. ICP-MS Calibration.** The NexION 300 ICP-MS was calibrated using synthetic Ra-226 standards that were cross-validated by gamma spectrometry. Both standard and collision modes of ICP-MS were evaluated. The standard mode was optimized for maximum ion transmission, resulting in higher Ra-226 intensity (Figure SI-1a). The collision mode with Kinetic Energy Discrimination (KED) used a nonreactive helium gas to remove polyatomic spectral interferences, thereby resulting in lower Ra-226 intensity (Figure SI-1b) but lower

interferences by matrix elements. Detection limit of Ra-226 was 100 pCi/L (i.e., 0.1 ng/L) with a relative standard deviation (RSD) of 45% and 67% for standard and collision modes, respectively (Figure SI-1). The RSD decreased to below 15% in the standard mode and 18% in the collision mode for Ra-226 concentration of 500 pCi/L and decreased even further with an increase in Ra-226 concentration (Figure SI-1). The detection limit was always well below the reported Ra-226 concentration in Marcellus Shale wastewater, which ranges from hundreds to tens of thousands pCi/L with a median of 2,460 pCi/L in Pennsylvania or 5,490 pCi/L in New York.<sup>4,5</sup> It is important to note that measurement of Ra-228 in MSW samples by ICP-MS is not feasible without preconcentration because the Ra-228 concentration typically ranges from 100–1,000 pCi/L ( $4.3 \times 10^{-4}$ – $4.3 \times 10^{-3}$  ng/L),<sup>5</sup> which is far below the detection limit of ICP-MS (0.1 ng/L).

#### 3.2. Impact of Matrix Elements on ICP-MS Analysis.

Matrix elements can affect the ICP-MS signal for Ra-226 via spectral overlap of polyatomic ions (e.g., <sup>88</sup>Sr<sup>138</sup>Ba, <sup>208</sup>Pb<sup>18</sup>O have an apparent signal with an *m/z* ratio identical to Ra-226)<sup>22</sup> and/or matrix induced signal intensity changes.<sup>38–40</sup> The latter effect is highly dependent on the ICP-MS operating conditions (e.g., gas flow rate, applied power) that impact the ionization equilibrium of the analyte.<sup>40</sup> Generally, matrix induced signal intensity change would suppress the target analyte signal at higher concentrations of matrix elements and higher plasma power. The increase in concentration of matrix elements decreases the ratio of Ra-226 to the total ions that are introduced into the skimmer orifice. As a result, the space charge effects on the target ion, such as Ra-226, are decreased and the signal is suppressed.<sup>41</sup> To evaluate the interference of matrix elements with Ra-226 measurement by ICP-MS, standard Ra-226 solutions with varying concentrations of matrix elements were prepared and compared with the standard Ra-226 in the background solution (i.e., 2% HNO<sub>3</sub>). Results in Table 1 show that the matrix elements have minimal impact on the apparent Ra-226 recovery (ratio of measured to actual Ra-226 concentration) as long as [Ca] < 30 mg/L, [Ba] < 10 mg/L

L, [Na] < 10 mg/L, and [Sr] < 5 mg/L. Ra-226 recovery obtained using the standard mode and collision mode varied from 93%–109% and 91%–108%, respectively. Ra-226 recovery decreased below 80% for samples containing more than 20 mg/L of barium.

**3.3. Method Development for Ra-226 Separation and Purification.** Radium can be easily separated from monovalent and divalent cations that have small hydrated ionic radii, but it is difficult to separate it from barium because of similarities in chemical properties.<sup>17,21</sup> The radium separation protocol developed in this study addresses these challenges by using two steps: 1) separation of radium, barium, and strontium from other cations and 2) separation of radium from the remaining barium and strontium. In this study, two methods, namely coprecipitation and solid-phase extraction were evaluated in the first step, while solid-phase extraction was used to separate radium from barium and strontium in the second step.

**3.3.1. Separation of Ra/Ba from Other Cations Using Coprecipitation.** Radium has similar chemical properties to barium and strontium and tends to coprecipitate with BaSO<sub>4</sub> or SrSO<sub>4</sub> even when solution is not saturated with respect to RaSO<sub>4</sub>.<sup>31</sup> The coprecipitation of Ra-BaSO<sub>4</sub> has been used to separate radium and barium from other matrix elements in a variety of environmental samples.<sup>7,28,32,33</sup> Those studies employed alpha spectrometry or liquid scintillation counting to analyze radium because they did not require further separation of radium and barium. As indicated earlier, the key drawback of alpha spectrometry is that it requires long detection time (i.e., several days), while liquid scintillation typically requires attainment of secular equilibrium, which takes about 3 weeks.<sup>32,33</sup>

Analysis of Ra-226 by ICP-MS requires separation of radium from barium to eliminate barium interference. Previous study converted BaSO<sub>4</sub> into BaCO<sub>3</sub> by boiling in saturated K<sub>2</sub>CO<sub>3</sub> solution<sup>34</sup> so that the carbonate mineral can be separated and dissolved in HNO<sub>3</sub> prior to further purification. A trial experiment with synthetic MSW was conducted to validate the effectiveness of this approach for high salinity solutions. Twenty mL of 1 M H<sub>2</sub>SO<sub>4</sub> was added to 2 mL of synthetic MSW and heated at 80 °C for 1 h to ensure complete coprecipitation of radium with BaSO<sub>4</sub>. Precipitate was then separated by filtration, washed with 20 mL of DI water, transferred into 15 mL of saturated K<sub>2</sub>CO<sub>3</sub> (i.e., 8.12 M), and boiled for 3 h. The resulting precipitate, which should be comprised mostly of BaCO<sub>3</sub>, was filtered, washed with DI water, and dissolved in 1 M HNO<sub>3</sub>. Concentrations of barium and radium in the solution were then measured to evaluate the chemical yield of BaCO<sub>3</sub> from BaSO<sub>4</sub> and associated radium recovery. Results showed that the chemical yield of BaCO<sub>3</sub> was 42.3% (*n* = 3), indicating incomplete transformation of BaSO<sub>4</sub> to BaCO<sub>3</sub>. As a consequence, radium recovery using this procedure was only 54.9% (*n* = 3). Therefore, this method for the separation of radium and barium does not seem effective for the high salinity samples including wastewater from unconventional gas extraction.

**3.3.2. Separation of Ra/Ba from Other Cations Using Solid-Phase Extraction.** A strong-acid cation exchange resin with high capacity and physical stability along with low eluent flow rate are desirable when trying to enhance the effectiveness and reproducibility of radium separation.<sup>30</sup> Thus, a highly cross-linked resin (Bio Rad AG 50W-X8, 8% divinylbenzene) with relatively small spherical particles (100–230 U.S. Mesh) and gravity driven eluent flow (average flow rate of 0.33 mL/min)

were widely used for separation of Ra/Ba from other cations<sup>21,25</sup> and were chosen for this study. Selectivity coefficients for different cations and hydrogen-form 50W-X8 resin in HCl solution are listed in Table 2. Selectivity coefficient

**Table 2. Selectivity Coefficient (*K*) for AG50W-X8 in HCl<sup>30</sup>**

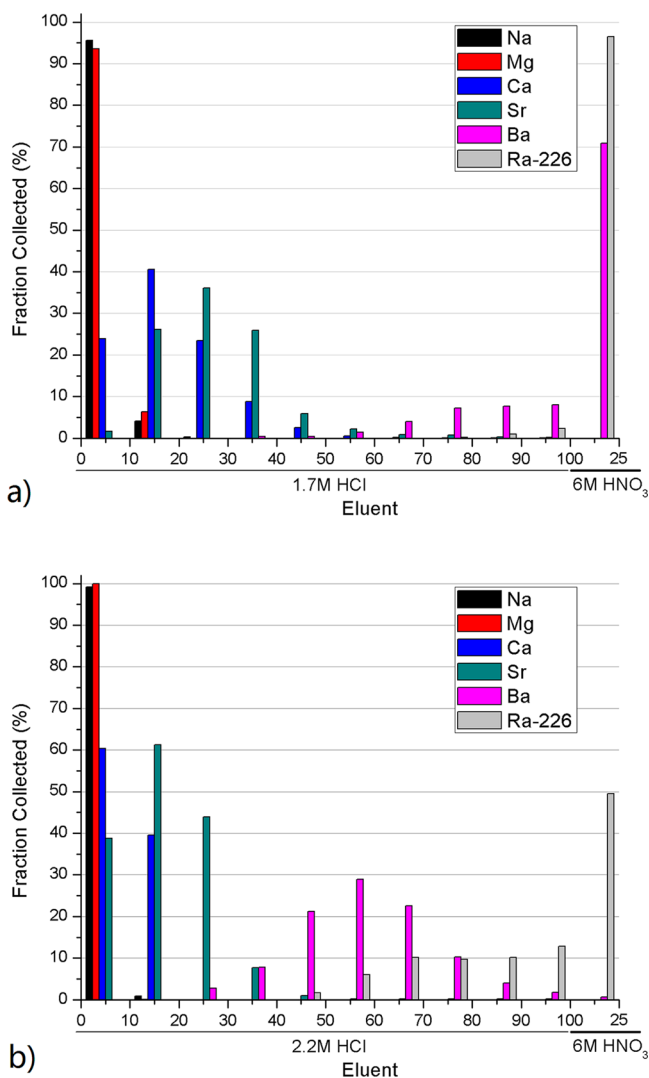
selectivity coefficient	HCl			
	0.1 M	0.5 M	1 M	2 M
Ba <sup>2+</sup>	>10 <sup>4</sup>	590	126.9	36
Sr <sup>2+</sup>	4700	217	60.2	17.8
Ca <sup>2+</sup>	3200	151	42.29	12.2
Na <sup>+</sup>	52	12	5.59	3.6
selectivity ratio $K_{H}^{Ba}/K_{H}^{Na}$	>192	49	22.7	10

for radium is not reported but should be close to or slightly higher than that for barium because of similar chemical properties and a slightly larger ionic radius of radium.

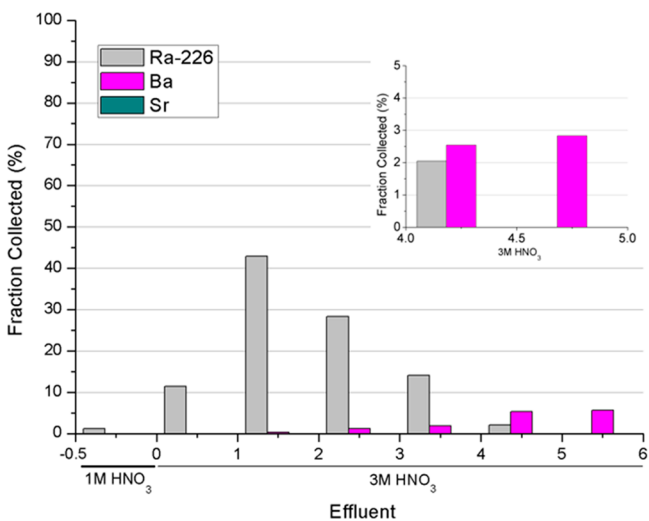
Based on the results shown in Table 2, it is expected that most of the radium and barium and some of the strontium can be effectively separated from other cations by this resin. Previous studies used 50W-X8 resin to separate radium and barium from other cations in groundwater with very high radium recoveries (e.g., 97%).<sup>16,21</sup> In order to validate the effectiveness of Ba/Ra separation for the dramatically more saline MSW sample, elution profiles of major cations and Ra-226 were developed in this study when 2 mL of acidified synthetic MSW was loaded on 4 mL of preconditioned 50W-X8 resin. The loaded resin was first washed with 100 mL of 1.7 or 2.2 M HCl followed by 25 mL of 6 M HNO<sub>3</sub>. The major cations and Ra-226 were measured in every 10 mL of the eluent. Results in Figure 1 indicate that either 80 mL of 1.7 M HCl (Figure 1a) or 40 mL of 2.2 M HCl (Figure 1b) will elute most of the sodium, magnesium, calcium, strontium, and some of the barium from the resin. Barium and radium remaining on the resin were then eluted with 25 mL of 6 M HNO<sub>3</sub>. The lower molarity eluent (i.e., 1.7 M HCl) was selected for further validation to maximize separation of radium from other cations and minimize radium loss.

**3.3.3. Separation of Ra-226 from Ba and Sr.** Previous work has shown that the uptake of alkali metal ions by a strong-acid exchange resin can be altered by the addition of crown ether functional groups.<sup>17,35</sup> The selectivity coefficient for radium on a Sr\*Spec resin that contains 1 M of 4.4'-(5)-bis(*tert*-butyl-cyclohexano)-18-crown-6 (crown ether) is more than 10 times lower than the selectivity coefficient for barium and strontium.<sup>36,37</sup> Previous studies have successfully separated radium from residual barium and strontium in groundwater and seawater using the Sr\*Spec resin.<sup>21,25</sup> Even though barium and strontium concentrations in those samples are more than 10 times lower than in MSW samples, the same resin (i.e., Eichrom Sr\*Spec resin) was used in this study to separate radium from remaining barium and strontium prior to ICP-MS analysis.

Two mL of synthetic solution containing 20 mM of barium, 1 mM of strontium, and 50,000 pCi/L of Ra-226, which is representative of the eluent that is collected from the separation step with 50W-X8 resin, was evaporated to dryness, dissolved in 0.5 mL of 1 M HNO<sub>3</sub>, and passed through 1 mL of Sr\*Spec resin. After that, 6 mL of 3 M HNO<sub>3</sub> was used to selectively elute Ra-226 from the resin. Concentrations of Ra-226, barium, and strontium were measured stepwise and are shown in Figure 2. These results indicate that 4.5 mL of 3 M HNO<sub>3</sub> effectively



**Figure 1.** Elution profiles for major cations and Ra-226 in synthetic Marcellus Shale wastewater with (a) 1.7 M and (b) 2.2 M HCl from 4 mL of preconditioned 50W-X8 resin.



**Figure 2.** Elution profile for Ba, Sr, and Ra-226 from Sr\*Spec resin with 0.5 mL of 1 M HNO<sub>3</sub> followed by 6 mL of 3 M HNO<sub>3</sub>.

elutes all Ra-226 from the Sr\*Spec resin. However, the separation between radium and barium is not complete because 5% of barium was eluted with Ra-226, resulting in close to 60 mg/L of barium in the combined eluent. A previous study showed that the presence of barium and strontium interferes with Ra-226 measurement during ICP-MS analysis and that even 5 mg/L of barium and 5 mg/L of strontium could amplify the Ra-226 signal by as much as 50%.<sup>18</sup> The breakthrough of barium occurred because the Sr\*Spec resin has a maximum capacity of approximately 0.24 meq/mL, and the working capacity should be between 10 and 20% of the maximum capacity to guarantee best performance.<sup>36</sup> Barium concentration in the Marcellus Shale wastewater is often very high<sup>2</sup> so that it could exceed the working capacity of Sr\*Spec resin, thereby leading to poor separation between barium and radium.

The impact of barium and strontium concentration on the performance of Sr\*Spec resin was evaluated using synthetic MSW samples containing barium concentrations up to 80 mM (11,000 mg/L) to represent the highest barium concentration reported in the Marcellus Shale wastewater<sup>2</sup> and Ra-226 concentration of 50,000 pCi/L. The results in Table 3 show

**Table 3.** Impact of Initial Ba and Sr Concentration on the Residual Concentrations in Purified Sample for ICP-MS Analysis

element	initial concn (mM)	percent in eluent		expected concn in purified sample <sup>a</sup> (mg/L)
		0–0.5 mL 1 M HNO <sub>3</sub>	0–4.5 mL 3 M HNO <sub>3</sub>	
Ba	10	0.0	0.4	4.8
Sr	1	0.0	0.0	0
Ba	20	0.0	5.4	148
Sr	1	0.0	0.0	0
Ba	40	0.0	16.2	891
Sr	1	0.0	0.0	0
Ba	80	0.0	24.2	2663
Sr	1	0.0	0.0	0

<sup>a</sup>Concentration in 2 mL of 2% HNO<sub>3</sub>.

that barium breakthrough during elution with 3 M HNO<sub>3</sub> can be substantial. If the initial Ba concentration in the sample is greater than 10 mM, barium concentrations in the final sample that would be injected in the ICP-MS will likely exceed 5 mg/L, which would cause strong interference during ICP-MS measurement. It is important to note that the radium recovery in 4.5 mL of 3 M HNO<sub>3</sub> was consistently close to 100%.

Barium concentration in the eluent was reduced via a second separation step with Sr\*Spec resin. After this second extraction step, the HNO<sub>3</sub> eluent was evaporated to dryness and redissolved in 2 mL of 2% nitric acid before analysis on ICP-MS. A schematic diagram of the optimized extraction procedure for the separation of radium from matrix elements in Marcellus Shale wastewater using a combination of 50W-X8 and Sr\*Spec resin is shown in Figure 3.

**3.4. Radium-226 Analysis in High Salinity Marcellus Shale Wastewaters.** In order to verify the analytical protocol developed in this study, four synthetic Marcellus Shale wastewater samples (Samples S1–S4) with varying salinities and concentrations of barium, strontium, and calcium were analyzed for Ra-226 using the sample purification procedure depicted in Figure 3. Composition of synthetic MSW was selected based on typical characteristics of Marcellus Shale

I. Separate Ba/Sr/Ra from other cations

II. Separate Ra from Ba/Sr

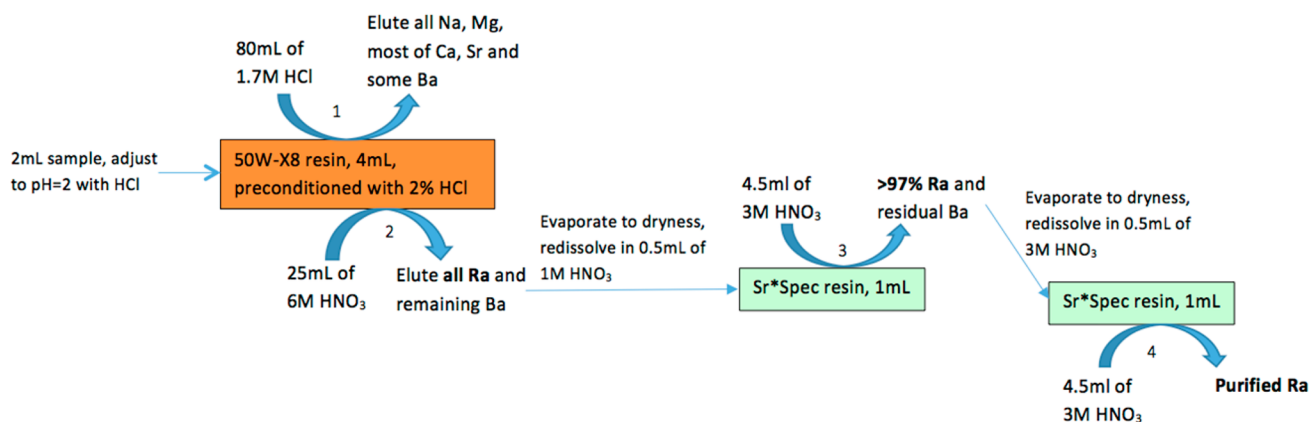


Figure 3. Schematic diagram of the separation protocol for Ra analysis by ICP-MS in Marcellus Shale wastewater.

Table 4. Comparison of Ra-226 Analysis in Synthetic MSW Samples by ICP-MS and Gamma Spectrometry<sup>a</sup>

sample	MSW composition (mg/L)					reference Ra-226 (pCi/L)	ICP-MS results			
	Na	Ca	Ba	Sr	TDS		standard mode		collision mode	
							Ra-226 recovery (%)	RSD (%)	Ra-226 recovery (%)	RSD (%)
S1	11,500	3,440	1,060	808	28,500	5,000	101	4	90	6
S2	23,000	6,880	2,120	1,620	57,000	5,000	99	5	94	2
S3	46,000	13,760	4,230	3,230	114,000	5,000	104	7	91	5
S4	69,000	20,640	6,360	4,850	171,000	5,000	107	6	104	1
S5	11,500	3,440	1,060	808	28,500	5,000	100	8	90	7
S6	46,000	13,760	4,240	3,230	114,000	5,000	95	5	91	8
S7	69,000	20,640	6,360	4,850	171,000	5,000	118	2	97	6

<sup>a</sup>Samples S1–S4 were purified by the procedure depicted in Figure 3; Samples S5–S7 were purified by the same procedure using regenerated Sr\*Spec resin.

wastewater.<sup>2</sup> Samples S5–S7 reflect the use of regenerated Sr\*Spec resin in the final step of Ra/Ba separation (2nd purification step with Sr\*Spec resin in Figure 3) to evaluate the possibility of reusing this relatively expensive resin. All samples were analyzed using ICP-MS in both standard and collision mode, and the results are compared with reference values for Ra-226 measured using gamma spectrometry in Table 4.

Ra-226 recovery for these 4 synthetic wastewater samples using the procedure depicted in Figure 3 varied from 95 to 107% for analysis in the standard mode and between 90 and 104% in the collision mode. These results indicate excellent agreement between the analytical procedure developed in this study and widely accepted protocol using gamma spectrometry. Furthermore, they suggest that it may be possible to reuse Sr\*Spec resin at least once to reduce the cost of this analytical procedure. The residual matrix elements in purified samples generally did not affect apparent Ra-226 recovery. The only exception was Sample S7 that had unusually high Ra-226 recovery, which is most likely due to high residual barium in the purified sample ([Ba] = 18 mg/L) caused by insufficient capacity of regenerated Sr\*Spec resin to retain barium.

Nine actual MSW samples collected at different locations or different stages of Marcellus Shale wastewater management cycle were analyzed to further validate the effectiveness of the proposed analytical procedure. Samples 1–3 were collected during the early stages of the flowback period and have relatively low salinity and low concentration of matrix elements. Samples 4–5 were collected from two MSW storage impoundments after several cycles of MSW reuse for hydraulic

fracturing, and samples 6–9 were collected from gas wells that have been in production for as long as 2.5 years. All samples were analyzed using ICP-MS and compared with Ra-226 measurement by gamma spectrometry in Figure 4. Excellent agreement between analytical results obtained using the two analytical methods suggest that the ICP-MS protocol developed in this study is accurate and robust for a variety of unconventional gas wastewaters that may be encountered in

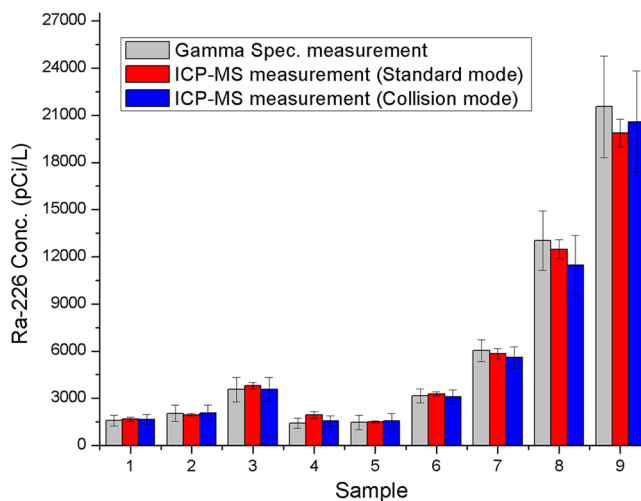


Figure 4. Comparison of Ra-226 analysis in field MSW samples by ICP-MS and gamma spectrometry.

different shale plays. Ra-226 recovery by the ICP-MS protocol in these real MSW samples was significantly higher than that of synthetic samples and ranged from 94–144% for standard mode and 90–118% for collision mode (Table SI-3). Such large variance in Ra-226 recovery is expected due to a large variance of gamma spectrometry measurement in this study (i.e.,  $\pm 11$ –31%).

The combined use of 50W-X8 and Sr\*Spec resins was very effective in separating sodium and strontium from both synthetic and field MSW samples regardless of salinity because their concentrations in the purified samples injected into the ICP-MS (residual concentrations) were consistently below 10 mg/L and 0.1 mg/L, respectively (Table SI-3). The residual calcium and barium concentrations were slightly higher, but most of the samples had residual calcium and barium concentrations below 30 mg/L and 10 mg/L, respectively. Based on the results shown in Table 1, such a low residual calcium and barium concentrations are not likely to cause significant matrix interference with ICP-MS detection. The only exception was the synthetic MSW Sample S7 that was prepared with reused Sr\*Spec resin and had the highest initial (6,360 mg/L) and residual barium concentration (18 mg/L). If the purified sample does not meet the interference criteria for other ICP-MS models, it may be necessary to further purify the sample by increasing the volume of HCl eluent (Figure 3, step 1) to decrease residual sodium and calcium concentration or by adding another separation step with Sr\*Spec resin to decrease residual barium concentration.

This study shows that rapid Ra-226 analysis using ICP-MS is feasible. Careful control of radium recovery in each step to optimize the solid-phase extraction protocol enabled the development of a reliable procedure to separate radium from the matrix elements with very high radium recovery. In comparison to conventional analytical methods for Ra-226 like alpha spectrometry, liquid scintillation counter, or gamma spectrometry, which are time-consuming (Table SI-2), the method developed in this study enables rapid and accurate analysis of Ra-226 even for samples with TDS as high as 415,000 mg/L. Average radium recovery in synthetic samples of Marcellus Shale wastewater was  $101\% \pm 6\%$  when ICP-MS was operated in the standard mode and  $97\% \pm 7\%$  when it was operated in the collision mode (Table 4). Although the initial results suggest that it may be possible to reuse Sr\*Spec resin at least once, additional evaluation is needed because of potential polyatomic interferences with Ra-226 analysis by ICP-MS in standard mode. However, it is possible to effectively remove this interference if ICP-MS is configured in the collision mode. The results obtained in this study indicate that it is critical to maintain residual barium and calcium concentrations in the purified sample injected in the ICP-MS below 30 and 10 mg/L, respectively to achieve accuracy and reproducibility of Ra-226 measurements.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Additional details on the operating conditions for ICP-MS, Ra-226 calibration curve, comparison of Ra-226 measurement methods, chemical composition of actual Marcellus Shale wastewater used in this study and calculated Ra-226 recovery. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: 1-412-624-9870. Fax: 1-412-624-0135. E-mail: [vidic@pitt.edu](mailto:vidic@pitt.edu).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

As part of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), a collaborative initiative of the NETL, this study was performed under Task Release No. TR 131, Project Activity No. 4.605.920.009.812.

## ■ REFERENCES

- (1) Vidic, R. D.; Brantley, S. L.; Vandenbossche, J. M.; Yoxtheimer, D.; Abad, J. D. Impact of Shale Gas Development on Regional Water Quality. *Science* **2013**, *340*, 6134.
- (2) Barbot, E.; Vidic, N. S.; Gregory, K. B.; Vidic, R. D. Spatial and Temporal Correlation of Water Quality Parameters of Produced Waters from Devonian-Age Shale following Hydraulic Fracturing. *Environ. Sci. Technol.* **2013**, *47* (6), 2562–2569.
- (3) Gregory, K. B.; Vidic, R. D.; Dzombak, D. A. Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements* **2011**, *7* (3), 181–186.
- (4) Warner, N. R.; Christie, C. A.; Jackson, R. B.; Vengosh, A. Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania. *Environ. Sci. Technol.* **2013**, *47* (20), 11849–11857.
- (5) Rowan, E.; Engle, M.; Kirby, C.; Kraemer, T. Radium content of oil-and gas-field produced waters in the Northern Appalachian basin (USA)—Summary and discussion of data. U.S. Geological Survey Scientific Investigations Report 2011-5135, U.S. Geological Survey **2011**.
- (6) Brantley, S. L.; Dave, Y.; Sina, A.; Paul, G.; Radisav, V.; Jon, P.; Garth, T. L.; Jorge, A.; Cesar, S. Water Resource Impacts during Unconventional Shale Gas Development: the Pennsylvania Experience. *Int. J. Coal Geol.* **2014**, *126*, 140–156.
- (7) U.S. Environmental Protection Agency. Method 903.0. Alpha-Emitting Radium Isotopes in Drinking Water.
- (8) U.S. Environmental Protection Agency. Method 903.1. Radium-226 in Drinking Water Radon Emanation Technique.
- (9) U.S. Environmental Protection Agency. Method 901.1. Gamma Emitting Radionuclides in Drinking Water.
- (10) Nelson, A. W.; May, D.; Knight, A. W.; Eitheim, E. S.; Mehrhoff, M.; Shannon, R.; Litman, R.; Schultz, M. K. Matrix complications in the determination of radium levels in hydraulic-fracturing flowback water from Marcellus Shale. *Environ. Sci. Technol. Lett.* **2014**, *1* (3), 204–208.
- (11) Köhler, M.; Preube, W.; Gleisberg, B.; Schäfer, I.; Heinrich, T.; Knobus, B. Comparison of methods for the analysis of  $^{226}\text{Ra}$  in water samples. *Appl. Radiat. Isot.* **2002**, *56* (1), 387–392.
- (12) Harvey, D. *Modern analytical chemistry*; McGraw-Hill: Boston, 2000.
- (13) Lawrie, W. C.; Desmond, J. A.; Spence, D.; Anderson, S.; Edmondson, C. Determination of radium-226 in environmental and personal monitoring samples. *Appl. Radiat. Isot.* **2000**, *53* (1), 133–137.
- (14) Escobar, V. G.; Tomé, F. V.; Lozano, J. C.; Sanchez, A. M. Determination of  $^{222}\text{Rn}$  and  $^{226}\text{Ra}$  in aqueous samples using a low-level liquid scintillation counter. *Appl. Radiat. Isot.* **1996**, *47* (9), 861–867.
- (15) Hancock, G. J.; Martin, P. Determination of Ra in environmental samples by  $\alpha$ -particle spectrometry. *Int. J. Radiat. Appl. Instrum., Part A* **1991**, *42* (1), 63–69.
- (16) Keisch, B.; Arnold, S. L. Sample preparation for low-level, alpha-particle spectrometry of radium-226. *Anal. Chem.* **1966**, *38* (13), 1969–1970.
- (17) Joannon, S.; Pin, C. Ultra-trace determination of  $^{226}\text{Ra}$  in thermal waters by high sensitivity quadrupole ICP-mass spectrometry

following selective extraction and concentration using radium-specific membrane disks. *J. Anal. At. Spectrom.* **2001**, *16* (1), 32–36.

(18) Horwitz, E. P.; Eietz, M. L.; Chiarizia, R. The application of novel extraction chromatographic materials to the characterization of radioactive waste solutions. *J. Radioanal. Nucl. Chem.* **1992**, *161* (2), 575–583.

(19) Leermakers, M.; Gao, Y.; Navez, J.; Poffijn, A.; Croes, K.; Baeyens, W. Radium analysis by sector field ICP-MS in combination with the Diffusive Gradients in Thin Films (DGT) technique. *J. Anal. At. Spectrom.* **2009**, *24* (8), 1115–1117.

(20) Varga, Z. Preparation and characterization of manganese dioxide impregnated resin for radionuclide pre-concentration. *Appl. Radiat. Isot.* **2007**, *65* (10), 1095–1100.

(21) Larivière, D.; Epov, V. N.; Reiber, K. M.; Cornett, R. J.; Evans, R. D. Micro-extraction procedures for the determination of Ra-226 in well waters by SF-ICP-MS. *Anal. Chim. Acta* **2005**, *528* (2), 175–182.

(22) Moldovan, M.; Krupp, E. M.; Holliday, A. E.; Donard, O. F. X. High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: a review. *J. Anal. At. Spectrom.* **2004**, *19* (7), 815–822.

(23) Larivière, D.; Epov, V. N.; Evans, R. D.; Cornett, R. J. Determination of radium-226 in environmental samples by inductively coupled plasma mass spectrometry after sequential selective extraction. *J. Anal. At. Spectrom.* **2003**, *18* (4), 338–343.

(24) Park, C. J.; Oh, P. J.; Kim, H. Y.; Lee, D. S. Determination of  $^{226}\text{Ra}$  in mineral waters by high-resolution Inductively Coupled Plasma Mass Spectrometry after sample preparation by cation exchange. *J. Anal. At. Spectrom.* **1999**, *14* (2), 223–227.

(25) Hsieh, Y.-T.; Gideon, M. H. Precise measurement of  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios and Ra concentration in seawater samples by multi-collector ICP Mass Spectrometry. *J. Anal. At. Spectrom.* **2011**, *27* (7), 1338–1346.

(26) Ghaleb, B.; Pons-Branchu, E.; Deschamps, P. Improved method for radium extraction from environmental samples and its analysis by thermal ionization mass spectrometry. *J. Anal. At. Spectrom.* **2004**, *19* (7), 906–910.

(27) De Muynck, D.; Huelga-Suarez, G.; Van Heghe, L.; Degryse, P.; Vanhaecke, F. Systematic evaluation of a strontium-specific extraction chromatographic resin for obtaining a purified Sr fraction with quantitative recovery from complex and Ca-rich matrices. *J. Anal. At. Spectrom.* **2009**, *24* (11), 1498–1510.

(28) Blackburn, R.; Al-Masri, M. S. Determination of radium-226 in aqueous samples using liquid scintillation counting. *Analyst* **1992**, *117* (12), 1949–1951.

(29) *Applications of liquid scintillation counting*; Horrocks, D., Ed.; Academic Press: 1974.

(30) Mizuike, A. *Enrichment techniques for inorganic trace analysis*; Springer-Verlag: 1983.

(31) Zhang, T.; Gregory, K.; Hammack, R. W.; Vidic, R. D. Coprecipitation of Radium with Barium and Strontium Sulfate and Its Impact on the Fate of Radium during Treatment of Produced Water from Unconventional Gas Extraction. *Environ. Sci. Technol.* **2014**, *48* (8), 4596–4603.

(32) Decaillon, J.-G.; Bickel, M.; Hill, C.; Alitzoglou, T. Validation of methods for the determination of radium in waters and soil. *Appl. Radiat. Isot.* **2004**, *61* (2), 409–413.

(33) Blackburn, R.; Al-Masri, M. S. Determination of radon-222 and radium-226 in water samples by Cerenkov counting. *Analyst* **1993**, *118* (7), 873–876.

(34) Ayrarov, M.; Krähenbühl, U.; Schneider, U. Fast determination of uranium and radium in waters of variable composition. *Czech. J. Phys.* **2006**, *56* (4), D219–D227.

(35) Dietz, M. L.; Chiarizia, R.; Horwitz, E. P.; Bartsch, R. A.; Talanov, V. Effect of crown ethers on the ion-exchange behavior of alkaline earth metals. Toward improved ion-exchange methods for the separation and preconcentration of radium. *Anal. Chem.* **1997**, *69* (15), 3028–3037.

(36) Horwitz, P. E.; Chiarizia, R.; Dietz, M. L. A novel strontium-selective extraction chromatographic resin. *Solvent Extr. Ion Exch.* **1992**, *10* (2), 313–336.

(37) Chabaux, F.; Othman, D. B.; Birck, J. L. A new Ra-Ba chromatographic separation and its application to Ra mass-spectrometric measurement in volcanic rocks. *Chem. Geol.* **1994**, *114* (3), 191–197.

(38) Olivares, J. A.; Houk, R. S. Suppression of analyte signal by various concomitant salts in inductively coupled plasma mass spectrometry. *Anal. Chem.* **1986**, *58* (1), 20–25.

(39) Tan, S. H.; Horlick, G. Background spectral features in inductively coupled plasma/mass spectrometry. *Appl. Spectrosc.* **1986**, *40* (4), 445–460.

(40) Olesik, J. W. Elemental Analysis Using ICP-OES and ICP-MS. *Anal. Chem.* **1991**, *63* (1), 12A–21A.

(41) Makishima, A.; Nakamura, E. Suppression of Matrix Effects in ICP-MS by High Power Operation of ICP: Application to Precise Determination of Rb, Sr, Y, Cs, Ba, REE, Pb, Th and U at  $\text{ng g}^{-1}$  Levels in Milligram Silicate Samples. *Geostand. Newslett.* **1997**, *21* (2), 307–319.